(54) Title: AUTOTHERMAL CATALYTIC STEM REFORMER
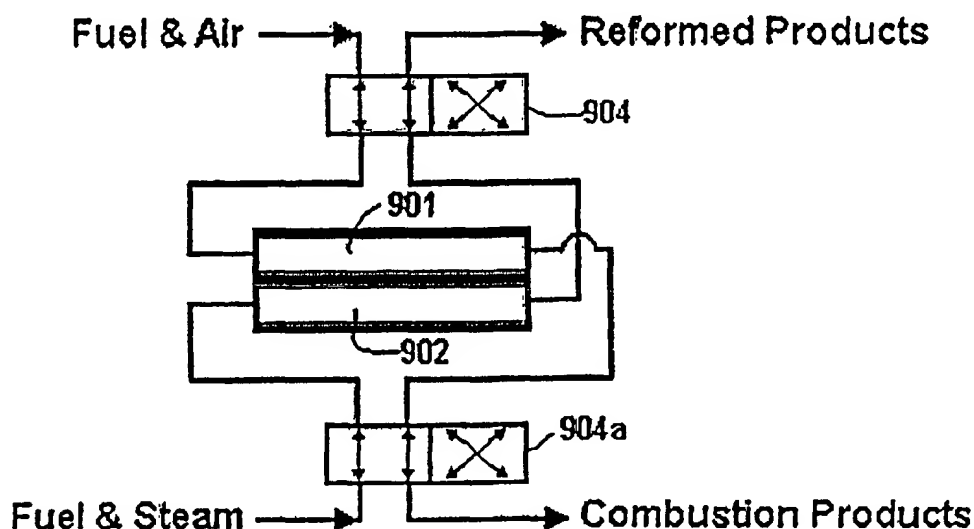
(57) Abstract: A compact steam reformer produces hydrogen to power a fuel cell, such as can be used in a vehicle. The steam reformer includes a first channel (902), at least partly coated with a stem reforming catalyst, and a second channel (901), at least partly coated with a combustion catalyst, the channels being in thermal contact with each other. Heat from the combustion is used in the steam reforming reaction. In one embodiment, the gas streams feeding the reforming and combustion channels pass through a valve (904, 904a) which reverses the gas streams periodically. The combustion channel becomes the reforming channel, and vice versa, so that carbon deposits in the former reforming channel are burned off. This arrangement enables the reforming reaction to continue indefinitely at peak efficiency.

AUTOTHERMAL CATALYTIC STEAM REFORMER

BACKGROUND OF THE INVENTION

This invention relates to the field of catalytic steam reforming of hydrocarbons to make hydrogen.

The hydrogen produced by the present invention may be used, for example, to operate a fuel cell. In a fuel cell, hydrogen is consumed during the process of producing electric power.

Steam reforming refers to the endothermic reaction whereby hydrogen is produced from methane, or from some other hydrocarbon. The steam reforming reaction, when the fuel is methane, is as follows:

$$CH_4 + H_2O \ ----> \ CO + 3H_2$$
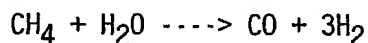
For reforming a C8 hydrocarbon, the reaction is:

$$C_8H_{18} + 8H_2O \ ---> \ 8CO + 17H_2$$

If the fuel cell is to be used to power a vehicle, the fuel cell, and the steam reformer used to supply hydrogen to the fuel cell, must be compact. Also, steps must be taken to reduce or eliminate the carbon monoxide products, which will quickly poison the membrane in the fuel cell. The present invention provides a practical, compact catalytic steam reformer, which can be used on a vehicle, or in other environments where space is severely limited.

A problem encountered in steam reforming is the deposit of carbon on the reforming catalyst. Although elemental carbon does not explicitly

appear in the equations shown above, it turns out that the steam reforming reaction does produce at least small amounts of carbon which, if allowed to build up, will eventually smother the catalyst and thereby render it useless. Carbon deposits are most likely to be produced when the fuel is a heavy hydrocarbon, such as a hydrocarbon having 12 or more carbon atoms per molecule. An example of such a heavy hydrocarbon is the fuel known as JP-8.

Moreover, to the extent that less than all of the hydrocarbon fuel is converted in the steam reforming reaction, some of the unconverted fuel will enter the fuel cell downstream of the reactor. When unconverted fuel appears in the fuel cell, carbon deposits are likely to form, and the fuel cell may be rendered inoperative. The smaller the fraction of fuel that is converted in the steam reformer, the greater the likelihood that the performance of the fuel cell will be harmed. That is why it is essential, in a commercial steam reformer, to operate continuously at or near maximum efficiency.

The present invention therefore includes an embodiment which insures that the fuel will be fully converted, or nearly so, in the steam reforming reaction.

Another problem with steam reformers is their tendency to accumulate sulfur. This is especially problematic with reformers using JP-8 and diesel fuel. The sulfur deposits tend to accumulate mostly in the coolest areas of the reactor. The present invention includes means for reducing or eliminating the problem of sulfur deposits.

SUMMARY OF THE INVENTION

In its simplest form, the steam reformer of the present invention comprises a reactor having a first strip of metal which is coated with a reforming catalyst on one side and with a combustion catalyst on the other side. This strip is confined between two uncoated strips which define a combustion channel on one side of the first strip and a reforming channel on the other side. Hydrocarbon plus steam flows through the reforming channel and hydrocarbon plus air flows through the combustion channel. Hydrocarbon is injected into the combustion channel at points along the length of the channel to maintain the temperature. Heat from the combustion channel is absorbed in the adjacent steam reforming channel, to drive the steam reforming reaction.

In a more preferred embodiment, the reactor comprises a stack of strips, defining a plurality of channels. Alternate channels are coated, at least partially, with a steam reforming catalyst, and the remaining channels are coated, at least partially, with a combustion catalyst. A mixture of hydrocarbon fuel and steam is directed into the steam reforming channels, and a mixture of hydrocarbon fuel and air is directed into the combustion channels. Additional hydrocarbon fuel is injected along the length of the combustion channels. As before, heat from the combustion channels is absorbed in the adjacent steam reforming channels.

In another preferred embodiment, the present invention comprises a plurality of stacks or modules, each constructed as described above. In this case, the additional hydrocarbon fuel can be injected before each stack, i.e. at the junction between successive stacks.

In another preferred embodiment, the steam reforming reaction is followed by a water-gas shift reaction, for converting carbon monoxide to

carbon dioxide and hydrogen. Each steam reforming channel (in the case of a single-module reactor) or each steam reforming channel of the last stack (in the case of a plurality of stacks connected in series) is connected to a channel which is at least partially coated with a water-gas shift catalyst. A cooling channel is provided adjacent to each such water-gas shift channel. In the water-gas shift channel, carbon monoxide reacts with water and is converted to carbon dioxide and hydrogen. The cooling channel reduces the temperature of the water-gas shift reaction so as to maximize the conversion of carbon monoxide to carbon dioxide.

In another embodiment, the invention includes an arrangement which compensates for the buildup of carbon deposits on the reforming catalyst. In this embodiment, the gas streams flowing into the reforming channel and the combustion channel are first directed through a two-position valve, or its equivalent. In its first position, the valve directs steam and fuel into the reforming channel, and directs air and fuel into the combustion channel. In its second position, the valve reverses the flow, and directs the steam and fuel into what was previously the combustion channel, and the air and fuel into what was previously the reforming channel. A second two-position valve, connected to operate simultaneously with the first valve, is located at the outlet end of the reactor, and maintains the relative positions of the gas streams. The same catalyst is used in both channels, and can comprise palladium and zirconia. The positions of the valves are controlled according to a measurement taken at the outlet end of the reactor. When the conversion ratio of the hydrocarbon (defined as the percentage of the hydrocarbon that is converted into carbon monoxide and hydrogen) falls appreciably below 100%, the unreformed hydrocarbon will appear in the effluent stream. When the concentration of the hydrocarbon in the effluent rises above a predetermined level, the system generates a

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signal to change the position of the valves. The steam reforming channel becomes the combustion channel, and the combustion channel becomes the steam reforming channel. Combustion in what was previously the reforming channel burns off the carbon deposits, which supplies part of the heat for the reforming reaction taking place in what was formerly the combustion channel. Thus, the steam reforming process can be conducted continuously and at or near peak efficiency.

In still another embodiment, the direction of gas flows through the channels are periodically reversed. This periodic reversal of flow is preferably accomplished by the same valve system that switches the channels. Flow reversal overcomes the problem associated with temperature gradients in the channel, as it insures that the regions that are relatively cool will periodically become the regions that are relatively hot. This arrangement minimizes the buildup of sulfur deposits in the reformer.

The present invention therefore has the primary object of providing a catalytic steam reformer.

The invention has the further object of providing an autothermal steam reformer, i.e. one which itself supplies the heat necessary to drive the steam reforming reaction.

The invention has the further object of providing a steam reformer which comprises a plurality of channels which are in intimate contact with each other.

The invention has the further object of providing a steam reformer for generating hydrogen for use in a fuel cell.

The invention has the further object of providing a steam reformer which is compact.

The invention has the further object of providing a steam reformer which is sufficiently compact that the reformer can be used in a vehicle.

The invention has the further object of providing a compact steam reformer which includes means for converting carbon monoxide produced by the steam reforming process, to carbon dioxide and hydrogen.

The invention has the further object of providing a compact and long-lived catalytic steam reformer for producing hydrogen for use in a fuel cell in a vehicle.

The invention has the further object of providing a method of generating hydrogen, through the use of a steam reformer.

The invention has the further object of providing a steam reformer which automatically regenerates itself by removing carbon deposits, and which therefore can be operated for extended periods with maximal efficiency.

The invention has the further object of providing a steam reformer which minimizes the formation of sulfur deposits.

The reader skilled in the art will recognize other objects and advantages of the present invention, from a reading of the following brief description of the drawings, the detailed description of the invention, and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 provides a simplified schematic diagram of a first embodiment of the steam reformer of the present invention.

Figure 2 provides a schematic diagram of an alternative embodiment of the present invention, wherein the reformer comprises a stack of channels in which combustion channels alternate with reforming channels.

Figure 3 provides a schematic diagram of a preferred embodiment of the invention, wherein a plurality of reformers, each of the type illustrated in Figure 2, are arranged in series.

Figure 4 provides an exploded perspective view of an embodiment of the present invention, wherein each reactor is formed from a stack of dimpled plates.

Figure 5 provides a graph showing an optimum cooling curve for the water-gas shift reaction conducted according to the present invention.

Figure 6 provides a schematic diagram of an embodiment of the present invention in which a steam reformer is combined with a water-gas shift reactor.

Figure 7 provides a schematic diagram of a plurality of steam reforming reactors, made according to the present invention, in which the flows in the reforming channels and the combustion channels are mutually countercurrent.

Figures 8a and 8b provide schematic diagrams of an alternative embodiment, wherein the identities of the combustion channel and reforming channel are periodically reversed, so that carbon deposits formed in the reforming reaction can be burned off.

Figure 9 provides a schematic diagram of another embodiment, wherein the combustion and reforming channels are switched, and wherein the directions of flow of the gas streams are periodically reversed.

DETAILED DESCRIPTION OF THE INVENTION

The simplest form of the invention is shown in the schematic diagram of Figure 1. Reactor 1 comprises three strips which define two adjacent channels. The first channel 2 is a reforming channel, i.e. it is where the steam reforming reaction occurs. The second channel 3 is a combustion channel.

In the embodiment shown, the middle strip 7 is coated on one side with reforming catalyst 4, and on the other side with combustion catalyst 5. Thus, first channel 2 has walls which are partially coated with reforming catalyst 4, and second channel 3 has walls which are partially coated with combustion catalyst 5. By "reforming catalyst" is meant a catalyst that promotes the steam reforming reaction discussed above.

A mixture of a hydrocarbon and steam is injected as shown at the left-hand side of the reforming channel. A mixture of a hydrocarbon and air is injected as shown at the left-hand side of the combustion channel. The hydrocarbon comprises fuel for the combustion.

The steam reforming reaction is endothermic, which means that it absorbs heat. The heat is supplied by the combustion which proceeds in the combustion channel, which is, in the embodiment of Figure 1, located on the other side of the strip.

In the arrangement of Figure 1, the middle strip 7 is coated, and the other strips are not coated. It is possible to use other coating schemes, whereby the steam reforming channels and/or combustion channels can be fully coated, or partially coated to varying degrees. All of such alternatives are included within the scope of the present invention.

If all of the fuel were injected at the inlet, the fuel would tend to burn there, causing a large temperature increase at the inlet. But the

steam reforming reaction is not fast enough to absorb all of the heat produced at the inlet, and the result would be an inefficient reformer. In a practical reformer, the conversion of the hydrocarbon must exceed about 95%.

The desired efficiency can be achieved by injecting hydrocarbon fuel at points along the combustion channel. Doing so will increase the combustion temperature to 800-900° C at each such point.

Figure 1 shows additional hydrocarbon fuel being injected into the combustion channel, at various positions along the channel, as indicated by arrows 6. Heat from the combustion is conducted through the common wall of the two channels, and this heat is absorbed by the endothermic steam reforming reaction. Note that additional fuel, but not air, is injected along the combustion path.

In the preferred embodiment, the hydrocarbon fuel injected into the reforming channel has the same composition as the fuel injected into the combustion channel. Thus, the two channels can be supplied with fuel from the same source. Catalytic combustion in the combustion channel supplies the heat to drive the reforming reaction.

Figure 2 provides a schematic diagram of another embodiment of the invention, having increased throughput. The reactor shown in Figure 2 includes a stack of strips, of which four are shown. The strips define channels, in which alternate channels are steam reforming channels, and the remaining channels are combustion channels. The steam reforming channels are at least partially coated with steam reforming catalyst, and the combustion channels are at least partially coated with combustion catalyst. The mixture of hydrocarbon and steam is injected into the reforming channels, i.e. the channels coated with the reforming catalyst, and the mixture of hydrocarbon and air is injected into the combustion channels.

As in Figure 1, hydrocarbon fuel is also added (without additional air), simultaneously, at spaced points along the length of the combustion channels, as indicated by the arrows. Combustion air is injected at one end of each combustion channel.

When one uses a stack of strips, such as in the embodiment of Figure 2, one must provide piping to deliver hydrocarbon and air, preferably from the same source, to each of the combustion channels, and to deliver hydrocarbon and steam to each of the reforming channels. Such piping is illustrated only schematically in Figure 2. Also, for clarity of illustration, the figure does not show the means for preventing the strips from nesting together. Such means could include dimples formed in the strips.

Figure 3 provides a schematic diagram of a preferred embodiment of the present invention, in which there are a plurality of reactors arranged in series. Each reactor, such as reactors 32 and 43, comprises a stack of strips. Only two such reactors are shown in Figure 3, but it is understood that further reactors could be provided. In each stack, alternate channels are coated, completely or partially, with a combustion catalyst 20, and the remaining channels are coated, completely or partially, with a reforming catalyst 21. For purposes of illustration, the combustion catalyst is symbolized by dashes, and the reforming catalyst is represented by x's.

Conduit 22 carries a mixture of hydrocarbon (HC) fuel and air, and is intended to supply the various combustion channels. Conduits 23 and 24 branch off from conduit 22, and supply other combustion channels with the fuel-air mixture. In practice, there are many more channels than illustrated, and there are a corresponding number of conduits to supply them.

Conduit 27 carries a mixture of hydrocarbon fuel and steam, and is intended to supply the various steam reforming channels. Conduits 28 and 29 branch off from conduit 27, and supply other reforming channels with the fuel-steam mixture. As is the case for the combustion channels, a practical reactor will have many more channels than the number shown in the drawings, and there will be a correspondingly increased number of conduits to supply fuel and steam to all of the reforming channels.

The fuel in the fuel-air mixture in conduit 22 derives ultimately from a source intended to supply the entire system, though the fuel-air mixture in conduit 22 may have passed through one or more reactor stages before arriving at the particular reactor shown. Both fuel and air enter the first stage. Additional fuel, but not air, is injected before each reactor stage, as symbolized by conduit 30. The fuel entering through conduit 30 comes directly from the source, which may be the same source which supplies all other fuel to the system, and has not passed through any reactor stages before reaching conduit 30. Thus, conduit 30 corresponds generally to the injection of fuel symbolized by the arrows disposed along the length of the reactors shown in Figures 1 and 2. Note that the additional fuel entering through conduit 30 is injected into the fuel-air mixture so that it is automatically distributed among the individual combustion channels.

On the output side of reactor 32, conduits 33 and 34 merge into conduit 35, to carry combustion products out of the system, or into the next reactor stage. Similarly, conduits 36 and 37 merge with conduit 38 to carry the products of the reforming reaction out of the system or into the next reactor stage. As before, a new injection of fuel, for combustion, is made through conduit 39, similar to conduit 30.

One difference between the embodiments of Figures 1 and 3 is that the fuel in Figure 1 is injected at various points along a single combustion

channel, whereas in Figure 3, the additional fuel is injected between adjacent reactors arranged in series. The result in both cases is essentially the same.

The diagrams of Figures 1-3 are not limited to a particular structure. Many different structures could be used to accomplish what is shown in these figures. One way to make a commercial reformer system is to combine a series of welded plate heat exchangers, such as those that are available from Tranter, Inc. Such an arrangement is shown in Figure 4, and described below.

Figure 4 shows a stack of heat transfer plates 51, 52, and 53. These heat transfer plates include dimples which prevent the plates from nesting. The heat transfer plates are held together between flat end plates 54 and 55. Also, the sides of the channels defined by the heat transfer plates are sealed by seals 56 and 57, which are metal pieces that close off the sides. Thus, the spaces between adjacent heat transfer plates comprise fully sealed channels. In accordance with the present invention, the channels defined by the plates are alternately coated, either fully or partially, with reforming catalyst and combustion catalyst. Suitable conduits are provided, on either end of the channels, to direct the gas flows in the manner dictated by Figures 1-3. These conduits are symbolized by ports 58, 59, 60, and 61, but for purposes of clarity, the diagram does not show connections between the ports and the channels. The above is only one of many ways by which the structure illustrated in Figure 3 can be realized in practice.

As noted above, the steam reforming reaction produces carbon monoxide. Carbon monoxide will poison the membrane in a fuel cell, even in very small concentrations. It is therefore necessary to follow the reforming reaction

with what is known as the "water-gas shift" reaction, which converts carbon monoxide to carbon dioxide, as follows:

$$CO + H_2O \longrightarrow CO_2 + H_2$$
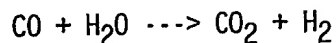
Note that one produces hydrogen both from the steam reforming reaction and from the water-gas shift reaction.

In the compact reactor of the present invention, the water-gas shift reaction is conducted in a channel that is just a continuation of the steam reforming channel. The catalysts can even be the same.

The water-gas shift reaction is exothermic, so that the equilibrium conversion to CO_2 and H_2 increases as the temperature decreases. The reaction rate also decreases as the temperature decreases. There is thus an optimum cooling curve, which maximizes the final conversion, when the outlet temperature has fallen to about 200° C, where the reaction rate is slow. This would include rapid cooling at high temperature and fast reaction rate, and slow cooling as the final temperature is approached. This optimum cooling curve is shown in Figure 5. In operating the water-gas shift reactor, one seeks to obtain a cooling profile as represented by this curve. To do so, one injects air into the cooling channel. This cools the channel so as to bring the reaction closer to equilibrium, so that the water-gas shift reaction goes nearly to completion.

Figure 6 provides a schematic diagram of a reactor which carries out both the steam reforming and the water-gas shift reactions. Reforming channel 101 is coated, at least partially, with reforming catalyst 102, on the left-hand side of the channel, and with water-gas shift catalyst on the right-hand side. The boundary between the reforming catalyst and the water-gas shift catalyst coincides with baffle 104 that separates the combustion channel 105 from cooling channel 106.

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In the embodiment wherein there are a plurality of reactors, as shown in Figure 3, the reactor of Figure 6 is located at the end of the series, i.e. at the outlet end of the system. That is, there is only one water-gas shift reactor. Note, however, that the reactor shown in Figure 6 may be much longer than any of the reactors depicted in Figure 3. The outlet of the water-gas shift channel comprises the output of the system, which contains hydrogen and carbon dioxide, with only traces of carbon monoxide.

In the embodiments discussed so far, the reforming stream and the combustion gas flow concurrently through the reactors. Alternatively, these two streams can be mutually countercurrent. Such an arrangement is shown schematically in Figure 7. Thus, for example, if the reforming channels are those identified by reference numeral 110, and the combustion channels are those identified by reference numeral 111, it is seen that the flow of combustion gas, in each reactor, is in the opposite direction to that of the flow of reforming gas. For simplicity of illustration, Figure 7 does not show a water-gas shift stage, but it is understood that such a stage can be appended to the system as described above.

A possible advantage of countercurrent flow is that it may create a smoother temperature profile through the series of exchangers.

It is an important feature of the present invention that the combustion channels and the steam reforming channels be in intimate thermal contact. Heat from the combustion channel must be able to flow unimpeded to an adjacent reforming channel to drive the reforming reaction. As illustrated in the drawings, the preferred way of insuring such intimate thermal contact is to have a system in which at least some of the metal strips are coated on one side with combustion catalyst and on the other side with reforming catalyst. Thus, only the metal of the strip separates a combustion channel from a reforming channel, and heat can freely flow

from the former to the latter.

A preferred steam reforming catalyst is rhodium or palladium, in combination with zirconia. Rhodium can be used as the catalyst for both the steam reforming reaction and the water-gas shift reaction. It is preferred to use platinum and/or palladium as the combustion catalyst.

A preferred catalyst system, for use in the present invention, is described below.

The source of the zirconia was a water-based solution of the oxynitrate $ZrO(NO_3)_2$, a commercial product, which contained 20% ZrO_2 and 20% HNO_3. The purchased solution was diluted with water. NH_4OH was added until the pH was 7.9. The exact value of the pH is believed not to be important.

A precipitate of $Zr(OH)_4$ was collected on a filter. A solution of rhodium nitrate was stirred into the wet filter cake. The mixture was stirred with a magnetic mixer, on a hotplate. Some water was evaporated during this process.

The resulting product was a thin "soup" of yellow color. This soup comprises a washcoat which could then be painted onto a metal strip with a brush. After being applied to the strip, each coat was calcined.

The rhodium nitrate solution contained excess HNO_3 which reacted with the $Zr(OH)_4$ to make the soup.

The same result was obtained by substituting palladium nitrate for the rhodium nitrate. In both cases, the coating was found to adhere to the strip very well.

Another embodiment of the invention, represented schematically in Figures 8a and 8b, overcomes the problem of carbon deposits that accumulate in the reforming channel. In this embodiment, a first gas stream

comprising air and fuel, and a second gas stream comprising steam and fuel, are directed to a two position valve 804. Valve 804 is located upstream of the inlet end of the reactor. Valve 804a, similar in construction to valve 804, is located downstream of the outlet end. Valves 804 and 804a are either mechanically linked, or controlled to operate together, so that they switch positions simultaneously.

In the position shown in Figure 8a, valve 804 directs the first stream, containing fuel and air, into channel 801 which comprises the combustion channel, and directs the second stream, containing fuel and steam, into channel 802, which comprises the reforming channel. Chromatograph 803 is configured to determine the concentration of fuel in the effluent of the reforming channel.

When carbon deposits accumulate in the reforming channel, the deposits form a barrier between the catalyst and the gases flowing in the channel, thereby making some of the catalyst unavailable to promote the reforming reaction, and thus reducing the conversion of hydrocarbon. Thus, as carbon deposits build up, the concentration of fuel in the effluent of the reforming channel increases. When this concentration exceeds a predetermined level, indicating that the conversion of fuel has fallen below a desired value, the chromatograph (or a computer connected to the chromatograph) signals valves 804 and 804a to switch to their other position, shown in Figure 8b. Element 803 can represent both the chromatograph and the computer, or other device, which generates a signal that controls the valves. More generally, element 803 represents any measurement and control device which measures the concentration of the unconverted hydrocarbon in the effluent stream of the reforming channel, and which controls the valves accordingly.

In Figure 8b, the first stream is now directed into channel 802, and the second stream is directed into channel 801. Thus, in Figure 8b, channel 802 becomes the combustion channel, and channel 801 becomes the reforming channel. The combustion in what formerly was the reforming channel burns off the carbon deposits, while the reforming reaction proceeds in the other channel. The heat generated by the burning of the carbon supplies part of the heat for the reforming reaction occurring in the adjacent channel.

Valve 804a restores the relative positions of the outlet streams. That is, valve 804a insures that, in the arrangement illustrated in Figures 8a and 8b, the combustion products will always be shown above the reformed products. It is important to preserve the relative positions of the streams, especially where multiple reactors are connected in series.

By switching the position of valves 804 and 804a, the identities of the combustion and reforming channels can be reversed in a matter of seconds. There need be no more than a momentary interruption of the reforming process. The steam reforming function is transferred to the other channel, while the original steam reforming channel is regenerated by burning off the carbon. Thus, the effective conversion ratio of the overall reactor will almost never drop appreciably below 100%, because there is always a fresh channel which can take over the reforming reaction. Thus, for practical purposes, the embodiment of Figures 8a and 8b comprises a steam reformer that operates without interruption, and always at or near peak efficiency.

To operate correctly, the embodiment of Figure 8a and 8b preferably uses the same catalyst on both sides of the strips, i.e. the same catalyst for combustion and for steam reforming. This catalyst can be palladium and zirconia, for example. A given channel supports either combustion or steam

reforming, depending on what gas stream is introduced into that channel. If the stream is air and fuel, combustion will occur. If the stream is steam and fuel, steam reforming will occur. It is also possible to use different catalysts in the combustion channel and the steam reforming channel, as long as both catalysts will support both combustion and steam reforming.

The embodiment of Figures 8a and 8b is especially useful in reforming heavy hydrocarbons, such as those having a carbon number in the range of 12-16 or greater, such as is found in the fuel known as JP-8. This embodiment is important in applications where even small deviations from 100% conversion cannot be tolerated, even near the end of a reforming cycle.

In another preferred embodiment, the measurement and control device 803 could include means for monitoring the time at which the valve positions are switched, and for calculating the time interval between movements of the valves. The faster the buildup of carbon deposits, the more frequently it will be necessary to switch the valve positions. Thus, a reduction in the time interval between valve operations is directly related to the rate of accumulation of carbon. The control device 803 is therefore programmed such that if the interval between valve operations falls below a predetermined level, the control device increases the proportion of steam entering the reactor. This control is indicated in Figures 8a and 8b by an additional dotted line 810 extending from control device 803 to the line which supplies the steam. The control device can adjust the proportion of steam by controlling a suitable valve (not shown in the figures), at a position in the line before the steam is mixed with the fuel. In general, an increase in the proportion of steam causes an

increase in the conversion, and therefore reduces the rate at which carbon is deposited.

The embodiment of Figures 8a and 8b can be generalized further. The apparatus could include a plurality of valves, similar to valves 804 and 804a, corresponding to a stack of channels, for changing the character of multiple selected channels from combustion channels to steam reforming channels, and vice versa.

Figure 9 shows another embodiment of the invention, wherein the identities of the combustion and reforming channels are switched, and wherein the direction of flow through the channels is reversed. Valves 904 and 904a are mechanically linked or operated together (similar to the operation of valves 804 and 804a of Figures 8a and 8b). In the position shown in Figure 9, fuel and air flows through valve 904 and enters channel 901, flowing from left to right. Channel 901 is therefore the combustion channel. The combustion products flow through valve 904a and exit at the lower right-hand portion of the drawing. Fuel and steam flows through valve 904a, and into channel 902, flowing from left to right. Channel 902 is therefore the reforming channel. The reformed products flow through valve 904 and exit at the upper right-hand portion of the drawing.

Now consider the situation when the valves are switched to their alternate positions. (The alternate valve position is not explicitly shown in Figure 9, but is implicit in the drawing.) Fuel and air passes through valve 904, and is directed to channel 902, flowing from right to left. Channel 902 therefore becomes the combustion channel. The combustion products flow through valve 904a, and exit at the lower right-hand side of the drawing. Fuel and steam passes through valve 904a, and is directed to channel 901, flowing from right to left. Channel 901 is now the reforming channel. The reformed products flow through valve 904, and exit at the

upper right-hand portion of the drawing.

Thus, the arrangement of Figure 9 simultaneously switches the combustion channel and the reforming channel, and also reverses the direction of flow through both channels. The configuration of the input and output streams is constant throughout; only the valve positions are changed. Thus, for example, the combustion products always appear at the lower right-hand side, and the reformed products always appear at the upper right-hand side.

The embodiment of Figure 9 has the advantage of removing sulfur deposits that may form at the low-temperature end of the reforming channel. Also, carbon deposits are likely to become deposited preferentially at one end or the other. When the direction of flow is reversed, the low-temperature end becomes the high-temperature end, and vice versa. Sulfur deposits that accumulated at the low-temperature end will now be vaporized from the catalytic surface when that portion of the channel becomes the high-temperature end. Similarly, carbon deposits that accumulated preferentially at one end are likely to be burned off more readily when the direction of flow is reversed.

In Figure 9, the same valves that cause the channel switching also cause the reversal of flow. The decision on when to switch channels is made in the same manner as shown in Figures 8a and 8b, using a measurement and control device similar to element 803 of the above-mentioned figures. For simplicity of illustration, the control device is not explicitly shown in Figure 9.

In theory, the times at which the flow is reversed, and the times at which the channels are switched, could be different and independent of each other. Such an arrangement would require a different valve configuration

than what is shown, but should be considered within the scope of the invention. But it is believed that the problem of sulfur deposition can be adequately solved by reversing the direction of flow at the same time that the channels are switched, and the arrangement of Figure 9 is therefore considered the preferred embodiment for providing both channel switching and flow reversal.

The choice of whether to use the embodiment of Figures 8a and 8b or the embodiment of Figure 9 depends on the length of the channel. If the channel is relatively short, the temperature gradient in the channel will be small, and there would be no need for flow reversal. In this case, one would choose the embodiment of Figures 8a and 8b. If the channel is long, it is more likely that the temperature will vary significantly along its length, and the embodiment of Figure 9 would be preferred. Moreover, the embodiment of Figure 9 could still be used even with a relatively short channel.

The present invention has a primary advantage of compactness. This advantage is achieved by providing combustion on one side of a strip and steam reforming on the other. Also, the use of a stack of multiple layers further enhances the ability of the reactor to work in a compact space. The compactness is further enhanced by providing the reforming and water-gas shift reactions in the same channel, and by providing the cooling air in what would otherwise be a continuation of the combustion channel, as shown in Figure 6.

The invention can be modified in various ways. The arrangement shown in Figure 4 is only one example of a realization of the structure illustrated schematically in Figures 1-3. Other steam reforming catalysts could be used instead of those mentioned above. Also, the catalyst coating may be applied by any of the many known techniques, such as painting the

coating onto the strip with a brush, vapor deposition, spray coating, or by other methods. Such modifications, which will be apparent to those skilled in the art, should be considered within the spirit and scope of the following claims.

What is claimed is:

1. A steam reformer, comprising:

a first channel having a wall which is at least partly coated with a steam reforming catalyst, and

a second channel having a wall which is at least partly coated with a combustion catalyst,

wherein the second channel is positioned sufficiently close to the first channel to permit heat transfer from the second channel to the first channel, and

wherein the steam reformer further comprises a plurality of means for introducing fuel into the second channel, said plurality of introducing means being disposed at intervals along a length of the first channel.

2. The steam reformer of Claim 1, wherein the first and second channels have inlet and outlet ends, and wherein the outlet end of the first channel is connected to a channel having a wall at least partly coated with a water-gas shift catalyst, wherein the outlet end of the second channel is connected to a cooling channel having means for introducing air into the cooling channel.

3. The steam reformer of Claim 1, wherein the steam reforming catalyst is selected from the group consisting of rhodium and palladium.

4. The steam reformer of Claim 2, wherein the steam reforming catalyst is selected from the group consisting of rhodium and palladium, and wherein the water-gas shift catalyst is the same catalyst as the steam reforming catalyst.

5. The steam reformer of Claim 4, wherein the steam reforming catalyst is impregnated into a washcoat of zirconia which is applied to a surface of the steam reforming channel.

6. A steam reformer, comprising:

a first channel having a wall which is at least partly coated with a steam reforming catalyst, and

a second channel having a wall which is at least partly coated with a combustion catalyst,

wherein the second channel is positioned sufficiently close to the first channel to permit heat transfer from the second channel to the first channel, and

wherein the first and second channels have inlet and outlet ends, and wherein the outlet end of the first channel is connected to a channel having a wall at least partly coated with a water-gas shift catalyst, wherein the outlet end of the second channel is connected to a cooling channel having means for introducing air into the cooling channel.

7. A steam reformer, comprising:

a) a plurality of metal strips, the strips being spaced from each other to define a plurality of channels for gas flow, each channel having an inlet end and an outlet end,

b) wherein some of said channels comprise steam reforming channels which are at least partially coated with a steam reforming catalyst,

c) wherein some of said channels comprise combustion channels which are at least partially coated with a combustion catalyst, and

wherein the steam reforming channels are interspersed with the combustion channels to allow heat from a combustion channel to flow into an adjacent steam reforming channel,

wherein the outlet end of each steam reforming channel is connected to a channel having a wall at least partly coated with a water-gas shift catalyst, wherein the outlet end of each combustion channel is connected to a cooling channel having means for introducing air into the cooling

channel.

8.   The steam reformer of Claim 7, wherein each combustion channel is separated from each cooling channel by a baffle.

9.   The steam reformer of Claim 7, further comprising a plurality of means for introducing fuel into each combustion channel, said plurality of introducing means being disposed at intervals along a length of each combustion channel.

10.   The steam reformer of Claim 7, wherein the steam reforming catalyst is selected from the group consisting of rhodium and palladium.

11.   The steam reformer of Claim 7, wherein the steam reforming catalyst is selected from the group consisting of rhodium and palladium, and wherein the water-gas shift catalyst is the same catalyst as the steam reforming catalyst.

12.   The steam reformer of Claim 11, wherein the steam reforming catalyst is impregnated into a washcoat of zirconia which is applied to a surface of the steam reforming channel.

13.   A steam reformer comprising a plurality of modules connected in series, each module comprising:

a first channel having a wall which is at least partly coated with a steam reforming catalyst, and

a second channel having a wall which is at least partly coated with a combustion catalyst,

wherein the second channel is positioned sufficiently close to the first channel to permit heat transfer from the second channel to the first channel.

14.   The steam reformer of Claim 13, wherein a first channel of one of said modules is connected to a channel having a wall at least partly coated

with a water-gas shift catalyst, and wherein a second channel of said one of said modules is connected to a cooling channel having means for introducing air into the cooling channel.

15. The steam reformer of Claim 13, further comprising means for introducing fuel separately to each module.

16. The steam reformer of Claim 14, further comprising means for introducing fuel separately to each module.

17. The steam reformer of Claim 14, wherein the steam reforming catalyst is selected from the group consisting of rhodium and palladium.

18. The steam reformer of Claim 14, wherein the steam reforming catalyst is selected from the group consisting of rhodium and palladium, and wherein the water-gas shift catalyst is the same catalyst as the steam reforming catalyst.

19. The steam reformer of Claim 17, wherein the steam reforming catalyst is impregnated into a washcoat of zirconia which is applied to a surface of the steam reforming channel.

20. A steam reformer comprising a plurality of modules connected in series, each module comprising a stack of strips defining a plurality of channels, wherein alternate channels are coated with a steam reforming catalyst and are designated steam reforming channels, and wherein the remaining channels are coated with a combustion catalyst and are designated combustion channels, and means for introducing fuel to the combustion channels of each module.

21. The steam reformer of Claim 20, wherein a steam reforming channel of one of said modules is connected to a water-gas shift channel having a wall at least partly coated with a water-gas shift catalyst, and wherein a combustion channel of said one of said modules is connected to a cooling channel having means for introducing air into the cooling channel, wherein

the cooling channel is located sufficiently close to said water-gas shift channel to cool said water-gas shift channel.

22. The steam reformer of Claim 20, wherein the modules are connected by conduits, and wherein the steam reformer comprises means for introducing fuel separately to at least some of said conduits.

23. The steam reformer of Claim 20, wherein the steam reforming catalyst is selected from the group consisting of rhodium and palladium.

24. The steam reformer of Claim 21, wherein the steam reforming catalyst is selected from the group consisting of rhodium and palladium, and wherein the water-gas shift catalyst is the same catalyst as the steam reforming catalyst.

25. The steam reformer of Claim 23, wherein the steam reforming catalyst is impregnated into a washcoat of zirconia which is applied to a surface of the steam reforming channel.

26. A steam reformer comprising a plurality of modules connected in series, each module comprising a stack of strips defining a plurality of channels, wherein alternate channels are coated with a steam reforming catalyst and are designated steam reforming channels, and wherein the remaining channels are coated with a combustion catalyst and are designated combustion channels,

wherein a steam reforming channel of one of said modules is connected to a water-gas shift channel having a wall at least partly coated with a water-gas shift catalyst, and wherein a combustion channel of said one of said modules is connected to a cooling channel having means for introducing air into the cooling channel, wherein the cooling channel is located sufficiently close to said water-gas shift channel to cool said water-gas shift channel.

27. A method of making hydrogen in a compact space, comprising:

a) directing a mixture of a hydrocarbon fuel and steam into a steam reforming channel which is at least partially coated with a steam reforming catalyst,

b) simultaneously directing a mixture of a hydrocarbon fuel and air into a combustion channel which is at least partially coated with a combustion catalyst, wherein the combustion channel is in thermal contact with the steam reforming channel, and

c) injecting additional hydrocarbon fuel at a plurality of points along the combustion channel.

28. The method of Claim 27, further comprising directing products of a steam reforming reaction, from the steam reforming channel, into a water-gas shift channel which is coated with a water-gas shift catalyst.

29. The method of Claim 28, further comprising cooling the water-gas shift channel by directing air into a cooling channel which is adjacent to the water-gas shift channel.

30. The method of Claim 27, further comprising selecting the steam reforming catalyst from the group consisting of rhodium and palladium.

31. The method of Claim 28, further comprising selecting the steam reforming catalyst from the group consisting of rhodium and palladium, and selecting the water-gas shift catalyst to be the same catalyst as the steam reforming catalyst.

32. The method of Claim 30, wherein the steam reforming catalyst is applied to a surface of the steam reforming channel by impregnating the steam reforming catalyst into a washcoat of zirconia.

33. A steam reformer, comprising:

a first channel having a wall which is at least partly coated with a steam reforming catalyst, and

a second channel having a wall which is at least partly coated with a combustion catalyst, wherein the second channel is positioned sufficiently close to the first channel to permit heat transfer from the second channel to the first channel, and

a valve for selectively directing a first stream comprising air and fuel and a second stream comprising steam and fuel into said first and second channels, wherein one of said first and second channels comprises a combustion channel and another of said first and second channels comprises a steam reforming channel, and wherein an identity of said channels is determined according to a position of the valve.

34. The steam reformer of Claim 33, further comprising a measurement and control device connected to measure concentration of at least one component of an effluent from one of said channels, the measurement and control device being operatively connected to the valve for controlling a position of the valve in response to a measurement of said concentration.

35. The steam reformer of Claim 33, wherein the valve is configured to reverse a direction of flow through said first and second channels.

36. The steam reformer of Claim 34, wherein the measurement and control device also measures a time interval between valve operations, and wherein the measurement and control device is connected to adjust a proportion of steam flowing into the reformer in response to a measurement of said time interval.

37. The steam reformer of Claim 33, further comprising a plurality of means for introducing fuel into the second channel, said plurality of introducing means being disposed at intervals along a length of the first channel.

38. The steam reformer of Claim 37, wherein the first and second

channels have inlet and outlet ends, and wherein the outlet end of the first channel is connected to a channel having a wall at least partly coated with a water-gas shift catalyst, wherein the outlet end of the second channel is connected to a cooling channel having means for introducing air into the cooling channel.

39.   The steam reformer of Claim 33, wherein the steam reforming catalyst is selected from the group consisting of rhodium and palladium.

40.   The steam reformer of Claim 38, wherein the steam reforming catalyst is selected from the group consisting of rhodium and palladium, and wherein the water-gas shift catalyst is the same catalyst as the steam reforming catalyst.

41.   The steam reformer of Claim 40, wherein the steam reforming catalyst is impregnated into a washcoat of zirconia which is applied to a surface of the steam reforming channel.

42.   A steam reformer, comprising:

a first channel having a wall which is at least partly coated with a steam reforming catalyst, and

a second channel having a wall which is at least partly coated with a combustion catalyst, wherein the second channel is positioned sufficiently close to the first channel to permit heat transfer from the second channel to the first channel, and

a valve for selectively directing a first stream comprising air and fuel and a second stream comprising steam and fuel into said first and second channels, wherein one of said first and second channels comprises a combustion channel and another of said first and second channels comprises a steam reforming channel according to a position of the valve,

wherein the first and second channels have inlet and outlet ends, and wherein the outlet end of the first channel is connected to a channel

having a wall at least partly coated with a water-gas shift catalyst, wherein the outlet end of the second channel is connected to a cooling channel having means for introducing air into the cooling channel.

43.   The steam reformer of Claim 42, further comprising a measurement and control device connected to measure concentration of at least one component of an effluent from one of said channels, the measurement and control device being operatively connected to the valve for controlling a position of the valve in response to a measurement of said concentration.

44.   The steam reformer of Claim 43, wherein the measurement and control device is connected to control a flow of steam into the reformer, and wherein the measurement and control device is programmed to compute a time interval between valve operations, and wherein the measurement and control device is programmed to adjust a flow of steam into the reformer in response to said time interval.

45.   The steam reformer of Claim 42, wherein the valve also comprises means for reversing a direction of flow through the channels.

46.   A steam reformer, comprising:

a)   a plurality of metal strips, the strips being spaced from each other to define a plurality of channels for gas flow, each channel having an inlet end and an outlet end,

b)   wherein some of said channels comprise steam reforming channels which are at least partially coated with a steam reforming catalyst,

c)   wherein some of said channels comprise combustion channels which are at least partially coated with a combustion catalyst, and

wherein the steam reforming channels are interspersed with the combustion channels to allow heat from a combustion channel to flow into an adjacent steam reforming channel,

further comprising a valve for selectively directing at least one first stream comprising air and fuel and at least one second stream comprising steam and fuel into said combustion channels and said reforming channels respectively, the valve comprising means for reversing a flow of said streams such that said at least one first stream is directed into a reforming channel and said at least one second stream is directed into a combustion channel.

47. The steam reformer of Claim 46, further comprising a measurement and control device connected to measure concentration of at least one component of an effluent from at least one of said channels, the measurement and control device being operatively connected to the valve for controlling a position of the valve in response to a measurement of said concentration.

48. The steam reformer of Claim 47, wherein the measurement and control device is adapted to measure a time interval between valve operations and to control a flow of steam into the reformer, wherein the measurement and control device adjusts the flow of steam in accordance with said time interval.

49. The steam reformer of Claim 46, further comprising means for reversing a direction of flow through said channels.

50. The steam reformer of Claim 46, wherein the outlet end of each steam reforming channel is connected to a channel having a wall at least partly coated with a water-gas shift catalyst, wherein the outlet end of each combustion channel is connected to a cooling channel having means for introducing air into the cooling channel.

51. A steam reformer comprising a plurality of modules connected in series, each module comprising:

a first channel having a wall which is at least partly coated with a

steam reforming catalyst, the first channel comprising a steam reforming channel,

a second channel having a wall which is at least partly coated with a combustion catalyst, the second channel comprising a combustion channel, wherein the second channel is positioned sufficiently close to the first channel to permit heat transfer from the second channel to the first channel, and

means for directing steam and fuel into said first channel of each module, and for directing air and fuel into said second channel of each module, and valve means for reversing a flow of said steam and fuel and said air and fuel such that each steam reforming channel becomes a combustion channel and each combustion channel becomes a steam reforming channel.

52. The steam reformer of Claim 51, further comprising a measurement and control device connected to measure concentration of at least one component of an effluent from at least one of said channels, the measurement and control device being operatively connected to said valve means for controlling a position of the valve means in response to a measurement of said concentration.

53. The steam reformer of Claim 52, wherein the measurement and control device also computes a time interval between valve operations, and wherein the measurement and control device is configured to adjust a flow of steam into the reformer in accordance with said time interval.

54. The steam reformer of Claim 51, wherein a first channel of one of said modules is connected to a channel having a wall at least partly coated with a water-gas shift catalyst, and wherein a second channel of said one of said modules is connected to a cooling channel having means for

introducing air into the cooling channel.

55. A steam reformer comprising:

a)   a steam reforming channel and a combustion channel, the steam reforming channel and combustion channels being in thermal contact with each other, and

b)   means for directing a first stream comprising a hydrocarbon fuel and air, and a second stream comprising a hydrocarbon fuel and steam, into a valve,

c)   the valve having a first position wherein the valve comprises means for directing the first stream into the combustion channel and the second stream into the reforming channel,

d)   the valve having a second position wherein the valve comprises means for directing the first stream into the reforming channel and the second stream into the combustion channel.

56. The steam reformer of Claim 55, wherein the valve also comprises means for reversing a direction of flow through said steam reforming and combustion channels.

57. The steam reformer of Claim 55, further comprising a measurement and control device connected to measure concentration of at least one component of an effluent from one of said channels, the measurement and control device being operatively connected to the valve for controlling a position of the valve in response to a measurement of said concentration.

58. The steam reformer of Claim 57, wherein the measurement and control device also computes a time interval between valve operations, and wherein the measurement and control device is configured to adjust a flow of steam into the reformer in accordance with said time interval.

59. A steam reformer comprising:

a)   first and second channels, the channels being sufficiently close

to each other so as to permit heat transfer between the channels, the channels being coated with a catalyst suitable for promoting combustion and steam reforming,

b) a valve connected to direct a first stream comprising fuel and air, and a second stream comprising fuel and steam, into said channels, wherein in a first valve position, the first stream is directed into the first channel and the second stream is directed into the second channel, and wherein in a second valve position the first stream is directed into the second channel and the second stream is directed into the first channel,

c) a measuring and control device connected to measure a concentration of a component of an effluent of the reformer, and to control the valve in response to said measurement.

60. The steam reformer of Claim 59, wherein the measuring and control device also comprises means for computing a time interval between valve operations, and for adjusting a flow of steam in response to said time interval.

61. The steam reformer of Claim 59, wherein the valve also comprises means for reversing a direction of flow of gases through said channels.

62. A method of making hydrogen, comprising directing a first mixture of a hydrocarbon fuel and steam, and a second mixture of a hydrocarbon fuel and air, into a valve having two positions, wherein the valve in a first position directs the first mixture into a steam reforming channel which is at least partially coated with a steam reforming catalyst and directs the second mixture into a combustion channel which is at least partially coated with a combustion catalyst, and wherein the valve in a second position directs the first mixture into a channel which is at least partially coated

with a combustion catalyst and the second mixture into a channel which is at least partially coated with a steam reforming catalyst, wherein the steam reforming channel and the combustion channel are sufficiently close to permit heat transfer between said channels,

further comprising measuring a concentration of an effluent from at least one of the channels, and controlling the valve in accordance with a measured concentration of said effluent.

63. The method of Claim 62, further comprising directing products of a steam reforming reaction, from the steam reforming channel, into a water-gas shift channel which is coated with a water-gas shift catalyst.

64. The method of Claim 63, further comprising cooling the water-gas shift channel by directing air into a cooling channel which is adjacent to the water-gas shift channel.

65. The method of Claim 62, further comprising periodically reversing a direction of flow of gases through said channels.

66. The method of Claim 65, wherein the reversing step is performed simultaneously with the controlling step.
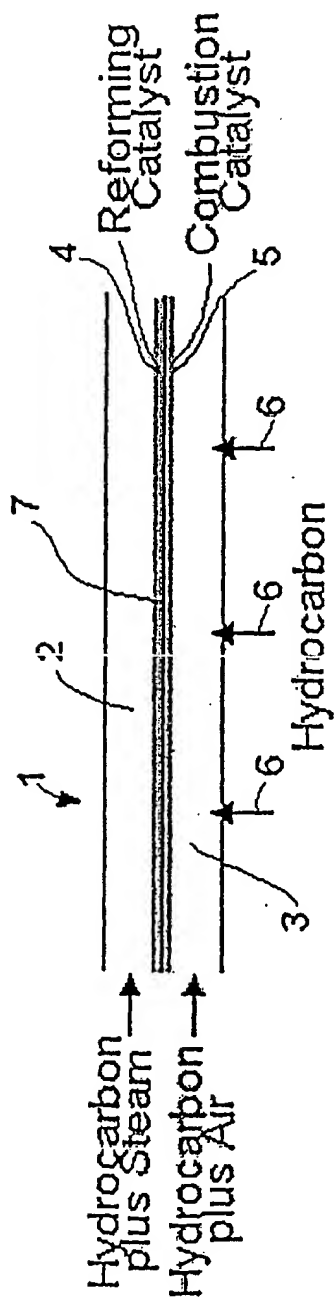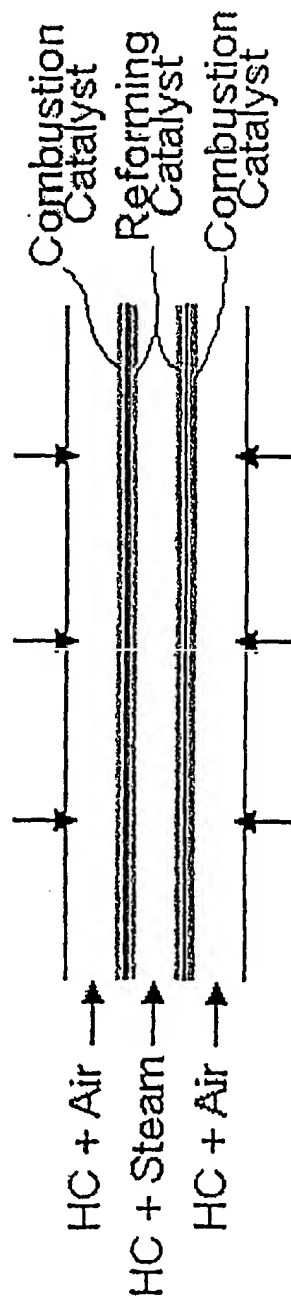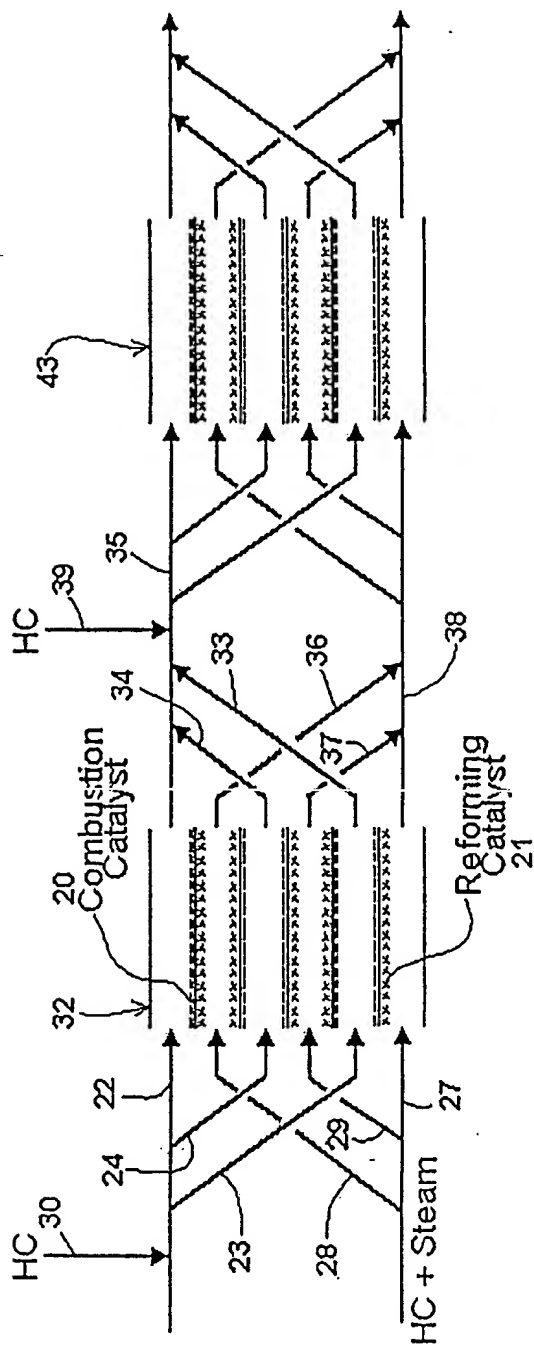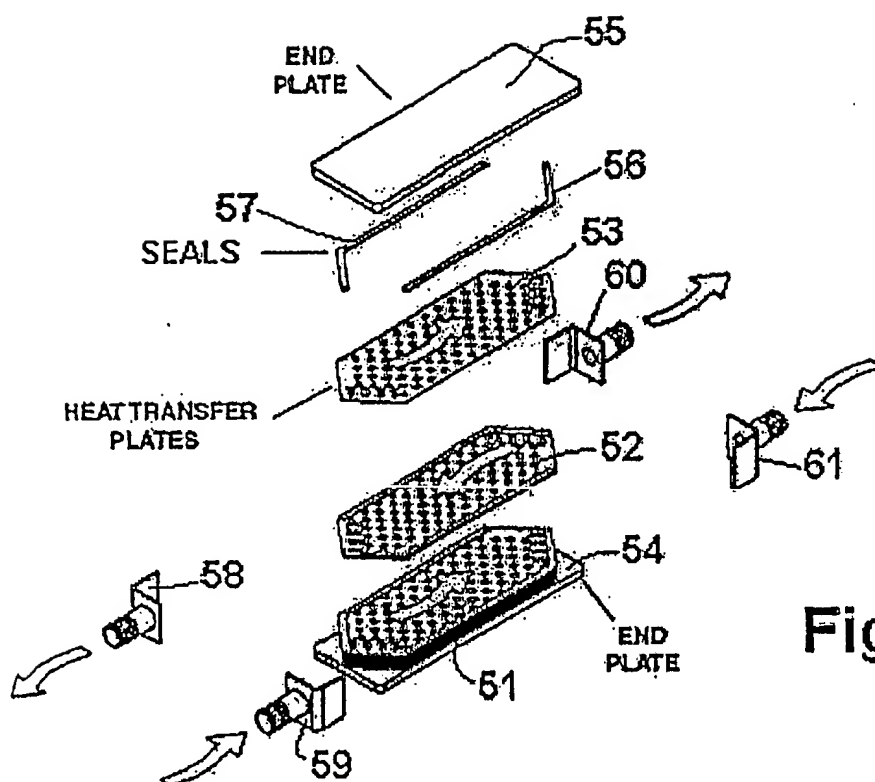
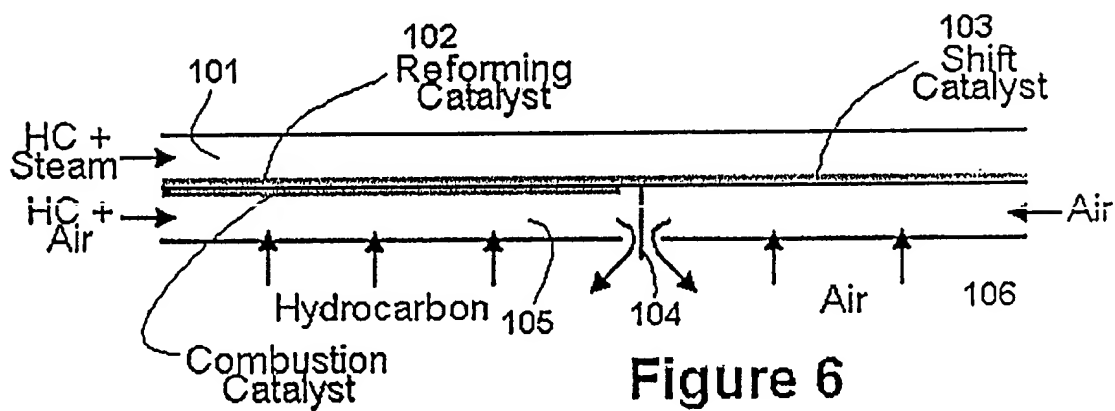Figure 1

Figure 2

Figure 3

Figure 4

Figure 5
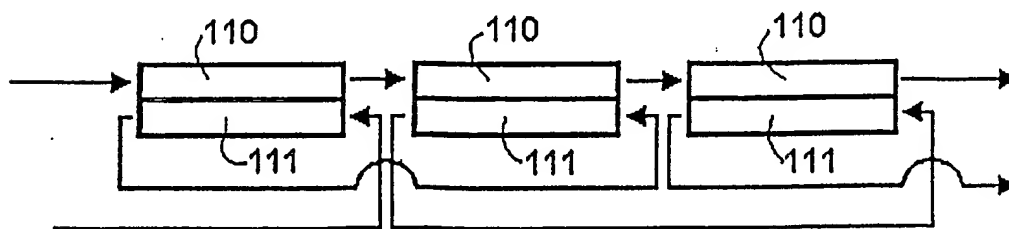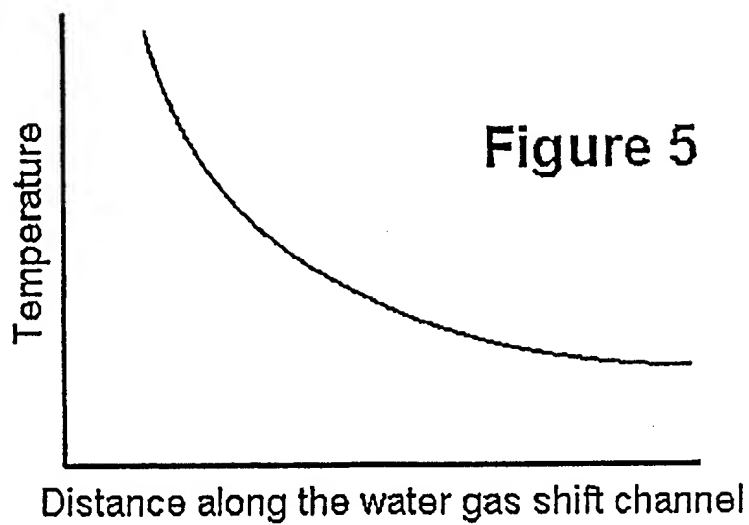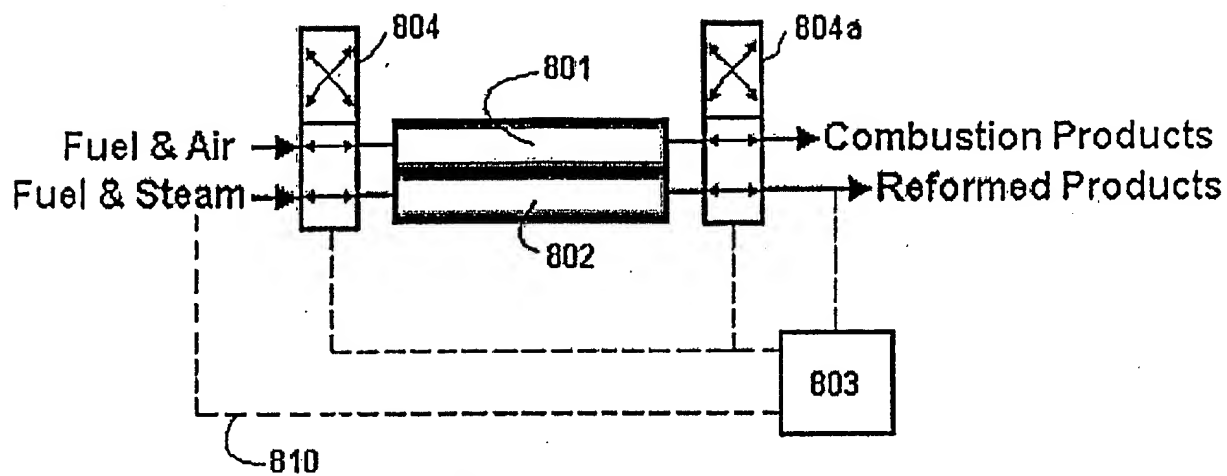
Figure 6

Figure 7

Figure 8a

Figure 8b

Fuel & Air ———→ ——————→ Reformed Products
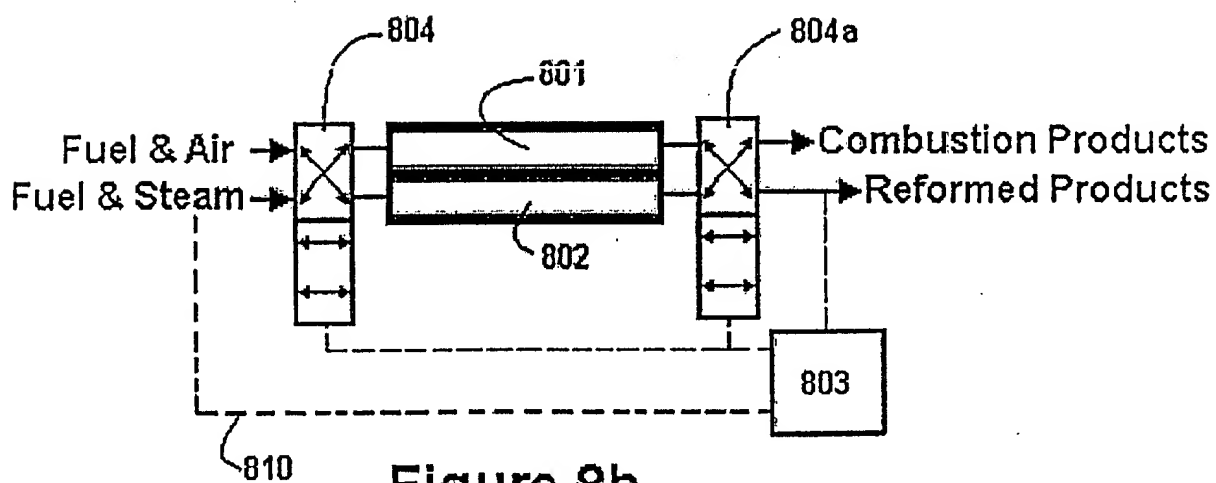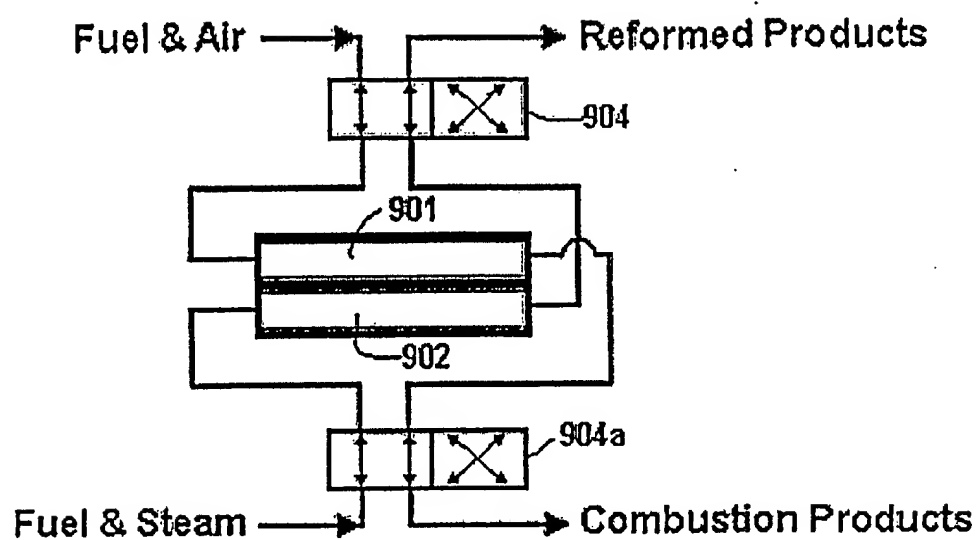
Figure 9

INTERNATIONAL SEARCH REPORT

A.	CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C10J 3/00
US CL : 48/61, 62R, 89, 119, 127.9, 198.7, 211, 214R; 422/188, 189, 190, 191, 193, 198, 211

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 48/61, 62R, 89, 119, 127.9, 198.7, 211, 214R; 422/188, 189, 190, 191, 193, 198, 211

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,214,867 A (HUNTER et al.) 29 July 1980 (29.07.1980), Fig. 2.	1-66
Y	US 5,167,865 A (IGARASHI et al.) 01 December 1992 (01.12.1992), Fig. 1-2.	1-66
Y	US 5,609,834 A (HAMADA et al.) 11 March 1997 (11.03.1997), Fig. 1-3	1-66
Y	US 5,672,629 A (HEIL et al.) 30 September 1997 (30.09.1997), Fig. 1-3.	1-66
A	US 5,248,566 A (KUMAR et al.) 28 September 1993 (28.09.1993)	1-66

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 August 2003 (28.08.2003)	**18 SEP 2003**
Name and mailing address of the ISA/US	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450	Basia Ridley Telephone No. (703) 308-0661
Facsimile No. (703)305-3230	

Form PCT/ISA/210 (second sheet) (July 1998)